

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

Two liquid are immiscible if they are completely insoluble in each other. Such a system actually consist of two phase, through it is usually referred to as a mixture. Example includes benzene and water, kerosene and water, ethanol and palm oil and etc. since by definition, immiscible liquid do not interact with each other in any whatsoever, they will evaporate completely independent of each other. In the other words, each liquid contributes its own its own characteristic equilibrium vapour pressure regardless of the presence of other liquid. Thus, the total pressure exerted by the mixture is the sum of the equilibrium vapour pressures. Besides, flows of two immiscible liquids are encountered in a diverse range of processes and equipments. In particular in petroleum industry, the mixtures of oil and water are transported in pipes over long distances. Accurate prediction of oil- water flow characteristics, such as flow pattern, water holdup and pressure gradient is important in many engineering applications. However, despite of their importance, liquid-liquid flows have not been explored to the same extent as

gas-liquid flows. In fact, gas-liquid systems represent a very particular extreme of two-fluid systems characterized by low density ratio and low viscosity.

Multiphase flows provide several mechanism for enhancing and extending the performance of single phase microfluidic systems. The long diffusion times and broad dispersion bands associated with single phase pressure-driven flow can be reduced by adding a second, immiscible, fluid stream. Multiphase flows form when two or more partially or not miscible fluids are brought in contact and subjected to a pressure gradient. The resulting flows display a rich phase behavior example as suspended droplets , bubbles, slugs or thin films. The flow behavior is independent on the relative flow rates of fluid phases involved, the resulting interaction between gravitational, interfacial, inertial and viscous forces and the wetting behavior of the channel wall. The alternating succession of immiscible fluid segments will play a particularly important role. Multiphase microchemical system generally take advantage of the large interfacial areas, rapid mixing and reduced mass transfer limitations to achieve improved performance relative to conventional bench scale system.

Non- edible oils, such as Pongamia Pinnata (Karanja or Honge), Jatropha (Jatropha or Ratanjyote), Madhuca ionduca (Mahua) and Castor oil have also been found to be suitable for biodiesel production (Yusuf et al.,2011). There are four primary techniques for biodiesel production: direct use and blending of raw oil, micro emulsions, thermal cracking and transesterification. Alkyl esters can be produced through transesterification of triglycerides, which are separated by immiscibility and higher density (Marchetti et al.,2007). Transesterification or alcoholysis is the reaction of a fat

oil with an alcohol (with or without catalyst) to form esters and glycerol. Moreover, transesterification of triglycerides with methanol and acid catalyst produce methyl ester and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. The step wise reactions are reversible and little excess of alcohol is used to shift the equilibrium towards the formation of esters.

## **1.2 Problem Statement**

Hydrodynamic behavior is the important phenomena in liquid-liquid flow system as it becomes a hindrance or mass transfer limitation if particular reactions are expected to occur. Knowledge about the fluid behavior is thus essential so that the process assuredly goes under the reaction limitation. In the study, the parameters such as Sauter diameter, drop size, dispersed phase hold up (phase inversion), emulsion and viscosity of the mixture is measured of the system of ethanol and palm oil. Capability of liquids to flow thru the aperture of inter-stage plate would be conceptualized using the bench mode as this preliminary before further investigation at the actual rig setup.

## **1.3 Research Objective**

The objective of this research is to elaborate flow behavior between ethanol and palm oil in various liquid-liquid systems.

## **1.4 Scope of the Study**

In order to achieve the objective of this research the scope of study has been determined:

1. Determination of sauter diameter and droplet velocity.
2. Liquid layer settlement study: concept of liquid holdup.
3. Batch hydrodynamic study using cylindrical viscometer without addition of catalyst (non-reactive approach).

## **1.5 Significance of Study**

A worthwhile goal of the fundamental study of settling mechanism is to reduce the scale of pilot work and cost involved by attempting to predict continuous settler capacity on the basis of a relatively small-scale batch test. Since, a batch test is inexpensive and simplest way of obtaining the relevant information, effort must therefore be put into a more fundamental understanding of the relation between batch and continuous settling. A set of batch tests over a wide range of initial conditions covering all the variables of a liquid-liquid system (dispersion height, drop size distribution, phase ratio and etc) should contain all the information required to design a continuous settler. Besides, the motion of liquid drops and their behavior in another liquid medium of infinite or restricted extent is of importance in liquid-liquid extraction

process, since in extraction equipment the contact between the phases as drops. Hence, knowledge of the hydrodynamic aspects should provide the basic information needed for the design of liquid-liquid contactors in which the drop size is related to the transfer efficiency and terminal velocity to the capacity of the equipment.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Liquid-Liquid Flow System**

Flows of mixtures of immiscible fluids are encountered frequently in the design of variety industrial process and equipments. Gas-liquid two phases flow represent a very “extreme” which has evoked extensive interest in the general area of multiphase flow in the last few decade. The resulting research into numerous aspects of various gas-liquid flows has contributed to a wide knowledge and understanding compared with that of other two-phase flows such as liquid-liquid flows. Depending of the flow condition, liquid-liquid mixtures from various flow pattern of interest, some of which have been identified experimentally (Charles et al 1961),. Furthermore, in principle, the behavior of liquid-liquid two phase flows is determined by the physical properties of the two

layers, the system geometry and associated flow pattern, as in gas-liquid mixtures (Russell et al 1959). However, as has been shown recently by author (Brauner et al 1991), the various concepts and result experienced in gas-liquid two phase flow cannot be readily translated to liquid-liquid flow prediction.

In a liquid-liquid extraction column, the effect of mass transfer on the column hydrodynamic behavior is of great importance and it should be taken into consideration in equipment design. The rate drop coalescence, which is strongly affected by the direction of mass transfer, becomes a decisive factor for the determination of the drop size. Since the rising velocity of the drops is function of their size, the drop residence time is also affected by the mass transfer. Larger drops will produced by higher coalescence rates, travel faster though the extractor and the result is lower residence times of the drops and therefore lower volume fraction (holdup) of the dispersed phase. Besides, the throughput before the onset of flooding and mass transfer coefficient rate is the most important parameter for design of column extractor(Tavlarides, 1993) .(Gourdon and Casamatta, 1991), in attempt to predict the influence of mass transfer direction on the operation of a pulsed sieve-plate pilot extraction column, reminded that, in the case of mass transfer from the drops to the continuous phase, every drop to drop collision result in coalescence. This assumption is probably true for a high mass transfer driving force. However, as the driving force becomes smaller and smaller, experimental result obtained that the coalescence efficiency decreases. Besides, more experimental results of the holdup and drop size distribution profiles in the presence of mass transfer along extractor obtained by novel techniques are presented. The holdup profile is

measured by an ultrasonic technique, while the drop size distribution is measured by a photomicrographic technique.

Meanwhile, solvent extraction has long a key operation in many processes for product purification and raw material recovery. Two phase liquid-liquid countercurrent column extractors have been widely use and have been extensively investigated. The recently published Handbook of Solvent Extraction provides a guide to the selection and design of such experiment. The design techniques outlined demonstrate that an experimental-empirical approach is employed in the absence of fundamental unifying theory. Moreover, it is recognized that the liquid flow pattern inside the contactors have significantly bearing on the column output. Specifically, large deviations from countercurrent plug flow, commonly known as back mixing model, lower the concentration driving force and reduce the column efficiency. This model have been developed for use in extractor design ( Sleicher et al., 1959 ) and also do not consider the special implications and distributed nature of the dispersed phase. For example, continual drop coalescence and redispersion result in the drop size distribution, which in turn causes a spread in the drop velocity and mass transfer rate. The design of an extraction column requires the determination of the column diameter and the column height or number of stages to achieve the desired separation. The hydrodynamic characteristics, especially the flood point and dispersed phase holdup of the extractor, determine the cross-section required to accommodate the desired flows without flooding. Having determined the column diameter, the mass transfer coefficients should next be considered in estimating the column height (Jahya et al., 2000).



In addition, the recently published Handbook of Solvent Extraction (Lo et al., 1983) provides a guide to the selection and design of such equipment. The design techniques outlined demonstrate that an experimental-empirical approach is employed in the absence of a fundamental unifying theory. It is recognized that liquid flow patterns inside the Font actors have a significant bearing on the column output. Specifically, large deviations from countercurrent plug flow, commonly known as backmixing, lower the concentration driving force and reduce the column efficiency. Backmixing models have been developed for use in extractor design (Sleicher, 1959; Miyauchi and Vermeulen, 1963). The models developed so far simply extend the backmixing models for a single phase and do not consider the special implications of the distributed nature of the dispersed phase. For example, continual drop coalescence and redispersion result in the drop size distribution, which in turn causes a spread in the drop velocity and mass transfer rates. It has been demonstrated (Olney, 1964) that for a mechanically agitated extractor creating a wide drop size distribution, monodispersed models do not describe with sufficient accuracy the mixing of the dispersed phase and the solute mass transfer (V. I. Kirou & J. C. Bonnet, 1988)

Mass transfer coefficients in extraction columns are generally obtained from the measured concentration profiles (or end concentrations) and values of operating variables by using an appropriate simulation model. Traditionally, columns were designed based on simple plug flow behavior, which does not incorporate the non-ideal flow effects caused by axial mixing. The presence of axial mixing results in a concentration jump at the inlet of each phase. The concentration driving potential for mass transfer is therefore

reduced, and hence, the extraction efficiency is adversely affected. It was reported that more than 70% of an extraction column height was used to cover the reduction in the mass transfer driving force because of axial dispersion. Extraction column operation is usually associated with changes in either or both of the phase flow rates. Generally, the feed flow rate and composition are allowed to change, each constituting a disturbance to the system, while the final raffinate composition is controlled by modulating the solvent flow rate. Phase flow rate changes, not only alter the concentration driving force throughout the column but also affect the rate of mass transfer since they are accompanied by corresponding changes in drop diameter, dispersed phase holdup and effective contact height. The height of the coalesced dispersed phase layer beneath a plate also depends on the flow rates of both phases and will thus be reflected on both the continuous and dispersed phase holdups on each plate. The interface level at the top column end is usually controlled by modulating either the top or the bottom product discharge rate. The inter-stage flow and holdup transients associated with changes in the phase inflow rates depend on the method of level control (R.S. Ettouney, 2012).

## **2.2 Hydrodynamic in Liquid- Liquid Flow System**

A perforated plate extraction column is one of the medium to meet the behavior of hydrodynamic properties with the liquid-liquid flow system which are used wide applications in a variety of chemical and metallurgical industries. Fairly reliable empirical correlations describing perforated plate hydrodynamics and mass transfer are very useful in an integrated modeling approach. The sequential application of such

correlations simplifies the computations involved in the design analysis of perforated plate columns and the development of steady state composition control models for existing columns. (Ettouney, 2007) state that steady state modelling of perforated plate extractive reactors enables the expression of the ratio between raffinate and feed compositions obtained in a column with a given number of plates in terms of three dimensionless parameters. (Ettouney and Rifai, 2011) study that the effective contact height is the difference between the plate spacing and the height of the coalesced layer which is obtainable from the pressure drop associated with the flow rates of both phases. Also, the dispersed phase holdup, slip velocity, and overall mass transfer coefficient are obtainable from standard hydrodynamics and mass transfer correlation(H. Achteilik, 2008).

Moreover, un-agitated perforated plate extraction columns are of simple construction and suitable for conducting extractive reactions. These columns are appropriate for systems which are characterized by low interfacial tension and thus do not require mechanical agitation for good dispersion. They are effective both with respect to liquid handling capacity and extraction efficiency. This is because mixing within the continuous phase is confined to the holdup between individual trays, it does not spread throughout the tower from stage to stage, and because the tendency to establish concentration gradients within the droplets is avoided as the dispersed phase droplets coalesce and are reformed at each tray. Unlike pulsed and agitated column contactors, the hydrodynamic characteristics of perforated columns are relatively simple and fairly predictable by a number of existing correlations. Besides, continuous phase on each plate is assumed to be well mixed and traversed by the dispersed phase droplets

assumed in plug flow. Although pilot testing maybe required for finalizing design details of extraction equipment, a simple model would be useful in preliminary process analysis because the effects of the basic design and operating conditions are not overshadowed by system complexity. The developed model enables the expression of the column behaviour in terms of meaningful dimensionless parameters. It is applicable in the evaluation of alternative design configurations as well as in the analysis of the steady state response of existing perforated plate extractors subject to feed flow and/or composition disturbances.(R.S. Ettouney 2006).

## **2.3 Fundamental Characteristics in Liquid- Liquid Flow System**

### **2.3.1 Sauter Diameter**

Once the drop size distribution has been determined, it was necessary to calculate the mean diameter. For liquid-liquid extraction, the surface area of drops controls the mass transfer through a liquid-liquid interface. The Sauter diameter ( $d_{32}$ ) is determined by using following equation:

$$D_{32} = \frac{\sum n_{pi} d_{pi}^3}{\sum n_{pi} d_{pi}^2}$$

Where  $n_{pi}$  is the number of drops and  $d_{pi}$  is the diameter of the droplet. Sauter diameter is defined as an average of particles size or the diameter of the sphere that has the same volume/ surface area ratio as a particle interest (Wikipedia). Knowledge of the Sauter diameter controls the liquid-liquid extraction equipment because it affects the dispersed volume hold up, the residence time of the organic drops and the mass transfer efficiency (S. Ousman 2010). Other than that, volume hold up and mean diameter determine the total interface surface available for mass transfer and consequently the overall mass transfer coefficient of the extraction.

### **2.3.1 Drop Size**

In an agitated vessel it is expected that the droplets continually coalesce and redisperse, so that a drop size distribution is produced. The mean size represent a dynamic equilibrium between the break-up and coalescence phenomena, with the characteristics of break-up predominating in dilute dispersions and those of coalescence in concentrated. In addition, it is known that the velocity of the liquid in an agitated vessel varies from place to place, being greatest in the immediate vicinity of the impeller blades ( Sachs and Rushton, 1954, Norwood and Metzner, 1960). Based on the theory of local isotropy (Kolmogoroff, 1941), expression have been derived for the maximum drop diameter that can be obtained in locally isotropic regions in baffled vessel. Two

mechanisms are apparent: one in which inertial effect predominates in the break-up drop and another in which viscous forces cause break-up.

### **2.3.2 Phase Inversion**

The identification of the dispersed phase under all conditions and the limits of stability of dispersions are very important in solvent extraction operations. Phase inversion is the transition from one phase dispersed to the other. It generally represented graphically by plotting the volume fraction of the dispersed phase in an heterogeneous mixture at inversion against the impeller speed. Figure 2.1, depicts a phase diagram which is typical of agitated heterogeneous liquid-liquid systems (Luhcing and Sawistowski 1971, Arashmid and Jeffreys 1980). While, figure 2.2, shows the phase inversion phenomena whereby the phases of liquid-liquid dispersion interchange such that the dispersed phase spontaneously inverts to become the continuous phase and vice versa under condition determined by the system properties, volume ratio and energy input (Arirachakaran 1989). Such an inversion characteristics demonstrates the existence of a hysteresis effect, represented graphically by two curves defining an ambivalent region. The system can only exist as aqueous dispersed/organic aqueous continuous below the lower curve. In between the two curves either aqueous or organic dispersed dispersions can be maintained and this region spontaneous phase inversion can take place. Since the consideration of plant performance usually dictate operation within the ambivalent range and the phase inversion concentrations. Phase inversion may lead to sudden increases in phase entrainment and flooding in gravity settler (Rowden et al.,1975).

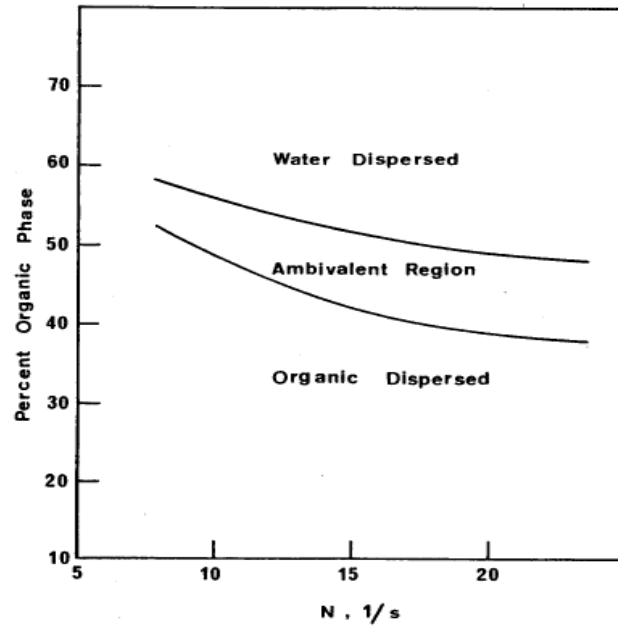


Figure 2.1: Typical inversion characteristic for oil/water dispersion

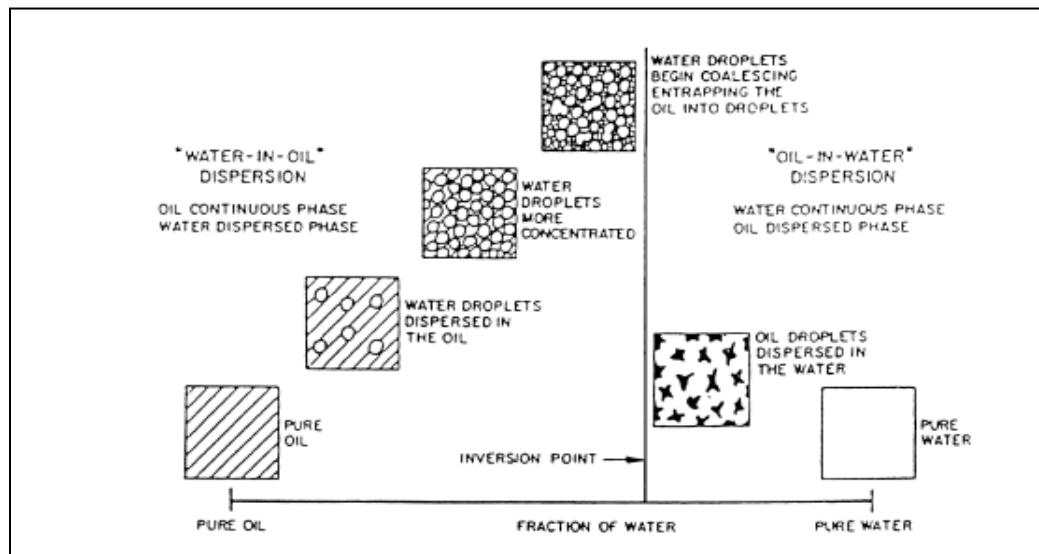


Figure 2.2: Phase inversion process for an Oil-Water dispersion system (taken from Arrachakaran, 1989)

### **2.3.3 The Formation of Emulsion in Liquid-Liquid System**

An emulsion is a mixture of two or more liquids that are normally immiscible. In the making of emulsions, hydrodynamic and interfacial phenomena interact. In order to make an emulsion, the energy is needed because the interfacial area between the two phases is enlarged, hence the interfacial free energy of the system increases. Besides, controlling factors in the formation of an emulsion are mechanical energy, agitation time, temperature, volumetric ratio between two phases, degree of dispersion of internal phase and presence of impurities surfactants (J.T. Davies 1964).

There are many ways of producing an emulsion and it usually achieved by applying mechanical energy through agitation, normally by using an homogenizer. Initially, the interface between the two phases is deformed and large droplets are formed. These droplet are subsequently broken up into smaller droplets by continuing agitation. One of the method normally used to break emulsions is gravity settling which is settling of emulsion is more rapid when the drop size larger and when the continuous phase viscosity is lower. For faster separation, heat can be applied to reduce the viscosity of continuous phase. Other than that, whether an emulsion of oil and ethanol turn into an “ethanol-in-oil” emulsion or “oil-in-ethanol” emulsion depends on the volume fraction of both phases and type of emulsifier. Emulsifiers and emulsifying particles tend to promote dispersion of the phase in which they do not dissolved very well.





## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Introduction**

In this chapter, there will be an explanation about the material used and detailed procedure that be going through in the experiment to achieve the objective of this research.

#### **3.2 MATERIAL**

##### **3.2.1 Chemical**

### **3.2.1.1 Palm Oil**

Palm Oil is one of the few highly saturated vegetable fats and does not contain cholesterol. Triglycerides form the major component and bulk of the glyceridic material present in palm oil with small amount of monoglycerides and diglycerides, which are artifacts of the extraction process. The fatty acid chains present in the palm oil triglycerides could vary in the number of carbons present in the chain and in structure. Besides, it is the variations in the structure and number of carbons in these fatty acids that largely define the chemical and physical properties of palm oil. The chain lengths of the fatty acid present in the triglycerides of palm oil fall within a very narrow range 12 to 20 carbons.

### **3.2.1.2 Ethanol**

Ethanol also known as ethyl alcohol, pure alcohol, grain alcohol or drinking alcohol is a volatile, flammable, colorless liquid. The molecular formula for ethanol is  $\text{CH}_3\text{CH}_2\text{OH}$  and the physical properties of ethanol stem primarily from the presence of its hydroxyl group and the shortness of its carbon chain. Ethanol's hydroxyl group is able to participate in hydrogen bonding, rendering it more viscous and less volatile polar

organic compound of similar molecular weight, such as propane. The boiling and melting point of ethanol are 78.37°C and -114 °C (Wikipedia).

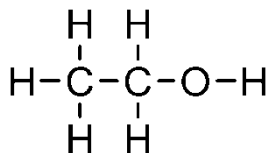


Figure 3.1: Formula structure of ethanol

### 3.2.2 Apparatus

The list of major apparatus that used in this research

- i) 500ml of measuring cylinder
- ii) 200ml, 500ml, 1000ml Beaker
- iii) Thermometer
- iv) Laboratory dropper
- v) Magnetic stirrer
- vi) Self-modified tube connected to syringe

vii) Camera

viii) Stopwatch

### **3.2.3 Equipments**

The list of major equipment used in this research

I Magnetic stirrer with hot plate

II Viscometer

#### **3.2.3.1 Viscometer**

The viscometer is an instrument used to measure the viscosity of fluid under one flow condition. Viscometric measurements, in general, deform a fluid sample in simple-shear geometry under controlled condition and measure its response in terms of torque, instrument dimensions, and geometrical constants. Thus, the attempt to “characterize” the fluid is made based on measuring a material parameter, namely the absolute viscosity and displaying the deformation (shear) rate dependence of viscosity, namely the relationship of shear stress as a function of shear rate.



Figure 3.2: Viscometer

### 3.3 Methodology

#### 3.3.1 Determination of Sauter Diameter and Droplet Velocity

Perforated plates play important part in extraction column. Dispersing makes one of the liquid contact with another liquid in form of droplets. It is to ensure the surface area much more bigger to contact with another liquid to extract the solute. In order to obtain large transfer area between raffinate and extract phases, one of the liquid must be dispersed into drops. For instance a dripping water tap, individual drops periodically leave the nozzle when volumetric flow rate of the dispersed phase is low.

### **3.3.1.1 Procedure of Determination Sauter Diameter and Droplet Velocity**

This experiment consists of two parts, which are in excess palm oil and excess ethanol. First, the experiment was carried out in 500 ml of palm oil. The modified tube using syringe was filled with ethanol (95%) and inserted into the measuring cylinder. The syringe was pressed until a few drops of ethanol forms and the diameter of each drop was measured from the photo taken by using mechanical ruler. Time taken for the drop to achieve the set point and distance also was estimated. For the next part, 500 ml of ethanol was prepared and filled dropper with palm oil. Then, the dropper was pressed until a few of drop of palm oil was formed in the ethanol solution. The diameter of droplet was measured from the photo taken by using mechanical ruler. Time taken and distance for the droplet to reach the set point was recorded.

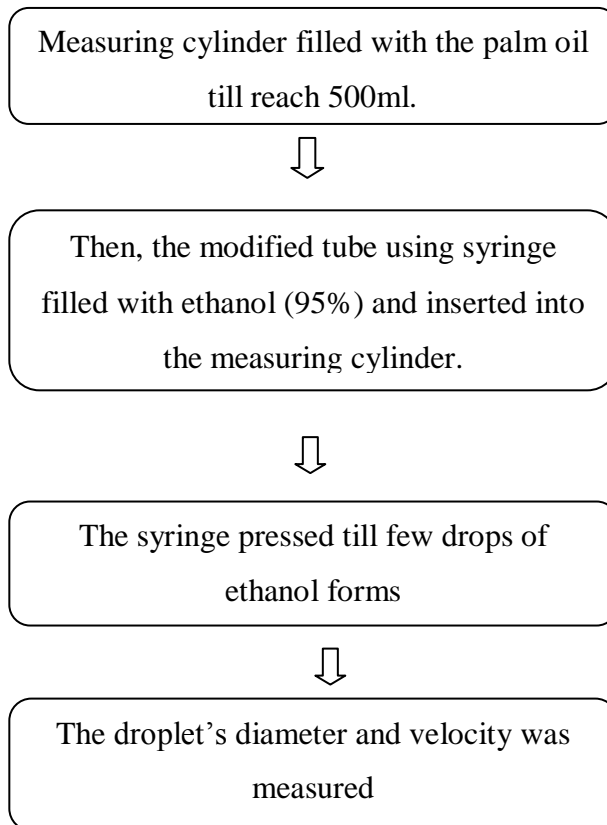


Figure 3.3: Process flow diagram of Sauter diameter and droplet velocity in excess oil

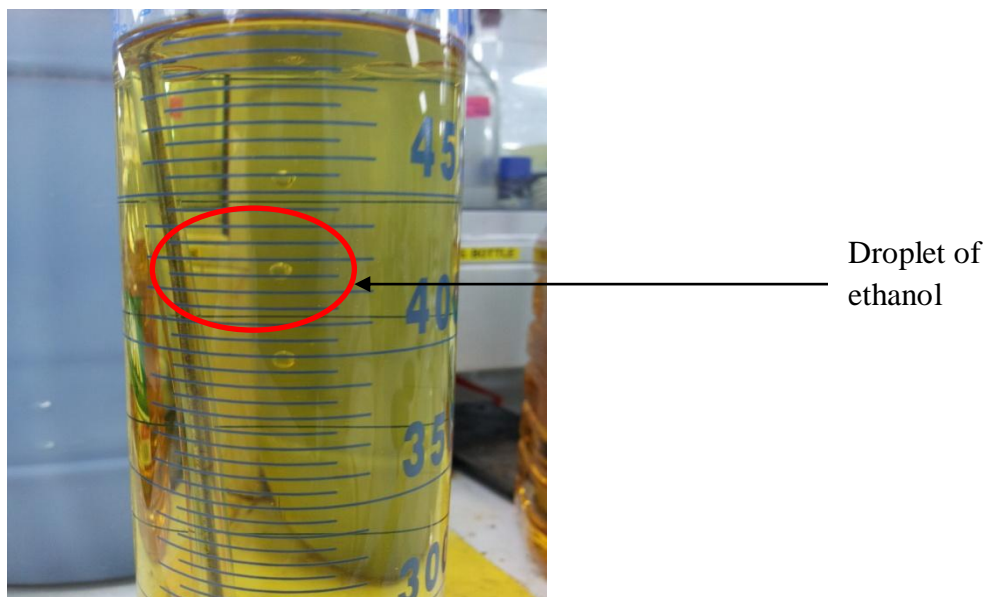


Figure 3.3: The droplet of ethanol in the palm oil